I. THE 1,4-DEHYDROGENATION OF VINYL ALCOHOLS

II. *PARA* ACYLATION OF AN AROMATIC KETONE

BY

ROBERT EVERETT FOSTER

A.B., Miami University, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGMENT

The author expresses his sincere appreciation to Professor R. C. Fuson for suggesting and directing these investigations.

I. THE 1,4-DEHYDROGENATION OF VINYL ALCOHOLS

Introduction

To study the effect of reduced hindrance at the *beta* carbon atom on the stability of enols similar to 1,2-dimesityl-1-propen-1-ol, it was proposed to reduce catalytically duryl α-phenylvinyl ketone. This compound, however, could not be synthesized. Instead, α,β-diphenylvinyl duryl ketone was used. An investigation was made of the behavior of this ketone toward reducing agents.

Experimental and Discussion

Condensation of benzyl duryl ketone with benzaldehyde gave a 70 per cent yield of α,β-diphenylvinyl duryl ketone. This compound absorbed one mole of hydrogen, but no enol could be isolated. The starting material was always recovered unchanged. To explain this phenomenon, it was assumed that the vinyl alcohol, although formed in the usual manner, was dehydrogenated immediately by the air. In support of this hypothesis, it was found that if the reduction mixture were allowed to stand for forty-eight hours, or if it were refluxed in an inert atmosphere for two hours, the saturated ketone, α,β-diphenylethyl duryl ketone, was formed. Evidently the enol had ketonized.

In view of the facts that 1,2-dimesityl-1-propen-1-ol can be dehydrogenated in the 1,4 manner by means of certain oxidizing agents,[1] and that small amounts of the α,β-unsaturated ketone can be obtained by the oxidative cleavage of this and similar enols,[2] the peculiar sensitiveness of 2,3-diphenyl-1-duryl-1-propen-1-ol can be explained. The vinyl alcohol now has a benzyl radical in place of the methyl group on the *beta* carbon atom. The benzyl radical would lose a hydrogen atom much more readily than would the methyl group, and thus enhance the ease of 1,4-dehydrogenation.

Three similar vinyl ketones—α,β-diphenylvinyl 2,4,6-triisopropylphenyl ketone, duryl α-phenyl-β-(*p*-chlorophenyl)-vinyl ketone, and mesityl α-phenyl-β-(*p*-chlorophenyl)-vinyl ketone were observed to exhibit the same behavior.

In connection with this work, a comprehensive survey of the methods of preparation of chalcones was made.

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II. *PARA* ACYLATION OF AN AROMATIC KETONE

Introduction

Speck has divided the action of Grignard reagents on highly hindered esters into three groups:[1] (I) condensation of aryl mesitoates with the Grignard reagent, (II) *ortho* alkylation and arylation of hindered diaryl ketones and (III) *para* acylation of mesityl aryl ketones.[2]

An example of this third group was studied.

Experimental and Discussion

Phenylmagnesium bromide condensed with *p*-tolyl 2,4,6-triethylbenzoate in butyl ether to give a 9 per cent yield of *p*-di-(2,4,6-triethylbenzoyl)-benzene and slightly higher yield of *p*-cresol. It appeared that 2,4,6-triethylbenzophenone was formed as an intermediate. To test this suggestion, the condensation of this ketone and the ester under the influence of the binary mixture Mg-MgI_2[3] was attempted. The expected product, *p*-di-(2,4,6-triethylbenzoyl)-benzene, was formed in 16 per cent yield along with *p*-cresol.

A mechanism for this unusual reaction has been presented.

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Vita

The writer was born in Salina, Kansas on January 27, 1919. He attended the schools of Lansing, Michigan and Oxford, Ohio, graduating from McGuffey High School, Oxford, Ohio, in June, 1936. In September of that year he entered Miami University, where he was granted the degree Bachelor of Arts in June, 1940. In the autumn of 1940, he matriculated in the Graduate School of the University of Illinois. He held an organic assistantship from 1940 to 1942, and since September, 1942 he has been a Special Research Assistant in Chemistry.

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